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MONITORING AMBIENT AIR VOCs USING CRYOGENIC AND ADSORBENT TRAP A CRITICAL EVALUATION

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INTRODUCTION

Analysis of ambient air volatile organic compounds (VOCs) is a complex task. This is due primarily to: 1. the wide variety of compounds of interest and 2. an ineffective means of analysis. The US EPA suggested a core set of three methods for sampling and analysis of ambient air VOCs (1). For the complete analysis of VOCs having boiling points from -10 to 200oC, the method suggested the use of a cryogenic analytical trap. This has been the method of choice, because it allows for the complete analysis of VOCs in a once-through type of operation. Of course, the use of a liquid N_2 cooled trap would imply the limited mobility of the system. This cryogenic trap also implies that atmospheric water vapor would be frozen in the trap, thus, clogging the trap and finally be desorbed into the GC. Therefore, creating many retention indices shift problems during the separation. In addition, with the equipment being operated at two extreme of temperatures, i.e., from - 196 to 220°C, it would always be a major contributing factor to the downtime.

One alternative to the cryogenic analytical trap is an adsorbent packed analytical trap. The advent of a new variety of adsorbents grants us the capability of adsorbing/desorbing compounds with a fairly wide range of boiling points. We

have therefore evaluated in this work, the validity of using an adsorbent analytical trap to do the analysis on the VOCs. Presented in this paper is the description of the objectives and results obtained from this work. Preliminary results were obtained using two adsorbent packed analytical traps. QA/QC data will be presented to demonstrate the advantages/disadvantages of using an adsorbent analytical trap for the VOC analysis.

EXPERIMENT

The adsorbent based analytical trap VOC thermal desorption / gas chromatograph / mass spectrometer system (TD/GC/MS) consists of a Tekmar LSC2000 thermodesorber (Cincinnati, OH), a Tekmar 4210 autosampler, a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and a Hewlett-Packard 300 series data station. The cryogenic trap VOC TD/GC/MS system consists of a Tekmar 5010 thermodesorber (Cincinnati, OH), a Hewlett-Packard 5890 GC (Palo Alto, CA), a Hewlett-Packard 5970 mass detector, and an Intel 80386/80387 based data station. Figure 1 illustrates a general block diagram of the two systems.

Two adsorbent analytical traps were used to concentrate the VOCs for the subsequent GC/MS analysis. Both analytical traps were obtained from Supelco Canada (Oakville, Ontario). The first one is a standard adsorbent trap (Supelco Cata. # 2-0321). The second analytical trap is a proprietary trap (2), courtesy of

Supelco Canada. Spiking mixtures were prepared using a modified gas mixing chamber (Lasale Glass, Barrie, Ontario). All data presented was obtained from both within run and between run experiments.

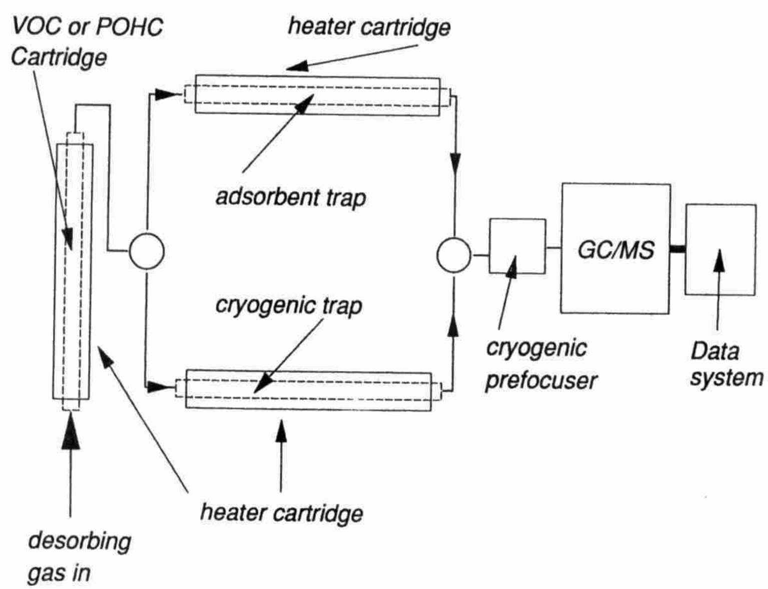

Figure 1. Block diagram of cryogenic and adsorbent based TD/GC/MS systems for the ambient air VOC analysis.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the total ion chromatogram (TIC) obtained from the cryo-

genic TD/GC/MS system. Figure 3 illustrates the TIC obtained from the adsorbent based TD/GC/MS system. Table 1 illustrates the QA/QC evaluation data obtained from the proprietary adsorbent trap TD/GC/MS system. Standard deviation data obtained from the standard adsorbent trap was too high to be useful. Table 2 illustrates prelimarily QA/QC data obtained from the cryogenic analytical trap TD/GC/MS system.

It is peculiar to note that we could not obtain useful data from the standard trap (Supelco cata.# 2-0321) which was capable of trapping the low boiling point volatile organic compounds under the purge and trap GC operation. The new trap (2) would allow us to trap the low boiling point VOCs in the TD/GC/MS system. Future studies are required to address this question.

CONCLUSION

We have demonstrated that applying adsorbent based TD/GC/MS system for the ambient air VOC analysis is feasible. Possibility of eliminate a cryogenic trap for the TD/GC/MS system offers a cost effective approach for the VOC analysis. Problems from liquid nitrogen related instrument downtime would have been eliminated, achieving a constant, maximized sample throughput.

REFERENCES

1. "Compendium of methods for the determination of toxic organic compounds in ambient air", R.M.Riggin, Battelle-Columbus Laboratories, Columbus, Ohio.
2. Robert Belardi, Supelco Canada, Oakville, Ontario, private communication.

TABLE 1. QA/QC DATA OBTAINED FROM AN ADSORBENT ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*	
		within	between
METHYL CHLORIDE (-23)	103.3	21.4	34.61
VINYL CHLORIDE (-13.9)	136.8	16.22	43.40
1,3-BUTADIENE (-4.5)	97.5	17.41	47.72
1,1-DICHLOROETHANE (31.9)	182.7	19.02	43.98
TRICHLOROMETHANE (61)	222.6	29.3	32.83
BENZENE (80)	131.8	33.03	42.78
BROMODICHLOROMETHANE (90)	295.65	31.07	43.04
TOLUENE (110)	129.9	23.62	34.11
1,2-DIBROMOMETHANE (131)	405.11	30.48	47.12
CHLOROBENZENE (131)	166.11	21.05	36.55
1,2-DICHLOROBENZENE (180)	195.0	9.48	18.48
NAPTHALENE (217)	174.3	16.61	14.57

* Presented in ±% to the spiked amount. The within run and between run data was obtained from 11 and 23 experiments, respectively.

TABLE 2. QA/QC DATA OBTAINED FROM AN CRYOGENIC ANALYTICAL TRAP TD/GC/MS SYSTEM FOR THE AMBIENT AIR VOC ANALYSIS.

COMPOUND NAME (B.P., °C)	AMOUNT SPIKED (ng)	STANDARD DEVIATION*
METHYL CHLORIDE (-23)	103.3	N/A
VINYL CHLORIDE (-13.9)	136.8	N/A
1,3-BUTADIENE (-4.5)	97.5	11.32
1,1-DICHLOROETHANE (31.9)	182.7	8.80
TRICHLOROMETHANE (61)	222.6	9.41
BENZENE (80)	131.8	10.2
BROMODICHLOROMETHANE (90)	295.7	18.9
TOLUENE (110)	129.9	6.73
1,2-DIBROMOMETHANE (131)	405.2	N/A
CHLOROBENZENE (131)	166.1	4.39
1,2-DICHLOROBENZENE (180)	195.0	4.81
NAPTHALENE (217)	174.3	8.23

* Presented in ±% to the spiked amount. Data obtained from 8 within run experiemnt.

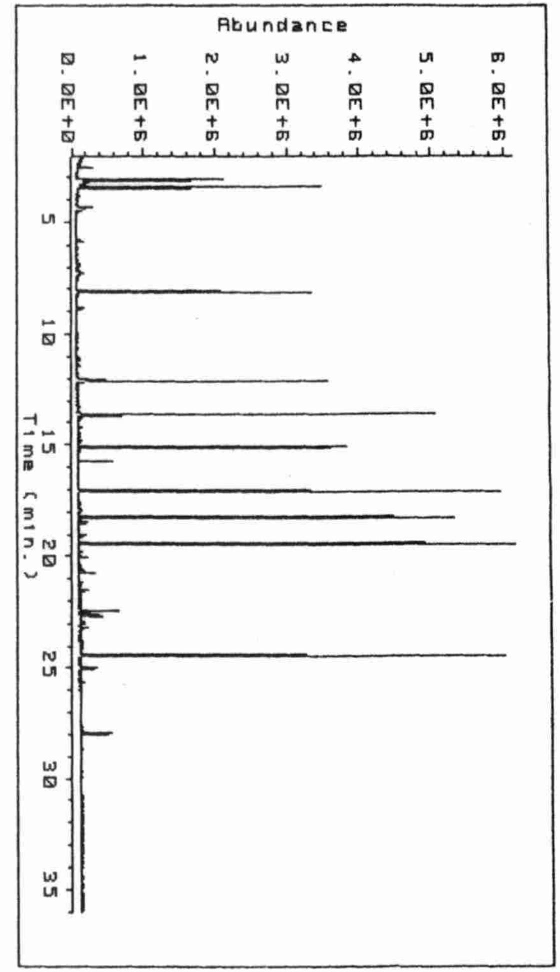

Figure 2: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system.

Figure 3: Total Ion Chromatogram obtained from the Ambient Air VOC TD/GC/MS system using Cryogenic Analytical Trap.